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Behavior of Tritium Accumulated on Materials Surface

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Abstract

Tritium release behavior and surface tritium behavior were separately examined for typical fcc and bcc metals by using tritium tracer techniques. Pure copper (Cu), iron (Fe), nickel (Ni) and molybdenum (Mo) were loaded with hydrogen including a trace amount of tritium and then immersed into water around room temperatures. Then, the tritium release rate into water was examined by a liquid scintillation counting technique and the surface tritium concentration by a tritium imaging plate technique.

The tritium release from the metals is attributed to the release of dissolved tritium by diffusion from the normal interstitial sites, and the first order desorption of trapped one with detrapping energies of 64 kJ mol^{-1}, 72 kJ $mol^{-1}$and 25 kJ mol^{-1} for Cu, Fe and Mo, respectively. Overall release behavior is varied depending on the ratio of

dissolved and trapped amounts of tritium.

Keywords

Tritium, Release, Diffusion, Trapping, Surface

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1. Introduction

It is well known that large amount of tritium is accumulated on surfaces of tritium loaded materials [1]. Such surface tritium accumulation is often attributed to adsorption/absoprtion at defects, surface oxide, precipitated impurities etc. and believed to largely influence solution, diffusion and permeation of tritium in the bulk. However, recent studies have shown that tritium release from austenitic stainless steels is likely to be not influenced by the densely accumulated tritium on the surface [2-4]. This motivates us to examine the effect of such surface accumulated tritium on behavior of tritium in the bulk. In the present study, the tritium release behavior and surface tritium behavior were separately examined for typical fcc and bcc metals by using tritium tracer techniques.

2. Experimental

Samples used here were sheets (10 x 10 x 0.1 mm^3) of pure copper (Cu), nickel (Ni), as fcc metals and iron (Fe) and molybdenum (Mo) as bcc metals. Nominal purity of all samples is above 99.9 %. The surfaces of the samples were polished with #2000 abrasive papers to remove the surface oxide layer and annealed in vacuum at 10^{-6} Pa, 873 K for 5 h in a quarts glass tube. Subsequently, hydrogen (H) including tritium (T,

T/H=1.25 x 10^{-4}) was loaded on the samples by a gas absorption method at 5.4 kPa, 873 K for 1 h. The loading procedure was finished by quenching the glass tube into liquid N_2 to prohibit T migration in the samples.

After the T loading, the samples were rapidly immersed into water (5 cm^{-3}) kept at 303, 323 and 353 K. Then an amount of T released into the water within 300 s was measured by a liquid scintillation counting (LSC) analyzer with time interval of 3600 s. T release rate was calculated by

$$J_i(t) = M_i / A_0 \Delta t \qquad (1),$$

where $J_i(t)$ and M_i are the T release rate and the amount of the released T at *i*th measurement, respectively. Δt = 300 s and A_0 is the sample surface area (10 x 10 mm^2). At each LSC measurement, the activity profile of T on the sample surface was also determined by a tritium imaging plate (TIP) technique which was conducted at 233 K for 24 h. The T concentration on the surface, $q(t)$, was then defined by

$$q(t) = \int_0^r \int_0^E \alpha(z, E)\, c(z, t)\, dE\, dz \qquad (2),$$

where $c(z,t)$ is the activity profile of T along z (depth) direction (see Fig. 3(a)), r is a maximum escaping depth of β electron with energy, $E_{Max.}=18.6\ keV$. $\alpha(z,E)$ is a factor containing the energy distribution of β electron, the interactions of β electron with materials, and the decay constant of T.

3. Results

3-1. Tritium release behavior

Figure 1 shows changes of the T release rate into water with time for (a) Cu, (b) Ni, (c) Fe and (d) Mo at 303 K, 323 K and 353 K. For Ni, the initial T release rate was the largest and rapidly decayed with time, while those for other metals show gradual change. The T release rate for Ni increased with temperature, and its decay became steeper. The rates for other metals also increased with temperature, but no significant changes appear in their time dependences.

Figure 2 (a) shows an integrated amount of T released into water for 2 x 10^4 s,

$$\boldsymbol{M}_{\boldsymbol{Exp.}} = \boldsymbol{A}_0 \sum_{\boldsymbol{i}=1}^{5} \boldsymbol{J}_{\boldsymbol{i}} \Delta \boldsymbol{t} \qquad (3).$$

The integrated amounts of the released T were larger in the order of Fe, Mo, Cu and Ni and increased with temperature.

3-2. Surface tritium concentration

Figure 3 (b) shows distributions of T activity on metal surfaces of Cu, Ni, Fe and Mo with black and white contrasts (higher activity black and lower white) obtained by

the TIP technique as indicated in Fig. 3 (a). Although the T activity was not uniform, Cu shows the highest in average.

The averaged surface T concentrations, *q(t)*, were determined by eq. (2) and were plotted with time in Fig. 4 for (a) Cu, (b) Ni, (c) Fe and (d) Mo. For all metals, the concentrations decayed gradually with no appreciable temperature dependence. From the difference of the surface T concentrations between two sequential measurements, the decay rates of the surface T were obtained. The rate was several kBq m^{-2} s^{-1} indicating good agreement in the order of magnitude with the release rate from Cu, Fe and Mo into water.

4. Discussion

Since T was loaded by the gas charging, T was likely dissolved in samples homogeneously. For homogeneously distributed T in a plane sheet of thickness, *l*, with the initial concentration of c_0, desorbed flux from the surfaces, *J(t)*, at temperature, *T* , is given by solving the Fick's second diffusion equation,

$$J(t) = \frac{2(4Dc_0)}{l} \sum_{n=0}^{\infty} \cos(2n+1)\pi \exp\left\{-\frac{(2n+1)^2 \pi^2 Dt}{l^2}\right\} \qquad (5),$$

where *D* is a diffusion coefficient of T presented by $D=D_0 exp(-E_D/RT)$. And the total released amount by diffusion for time, t_1, is given by

$$M_{Calc} = A_0 \int_{t=0}^{t_1} J(t)dt \qquad (6).$$

In Fig. 1, we have compared the experimental data with *J(t)* calculated with using the literature data of c_0 at 873 K and 5.4 kPa and *D* of protium (H) for each metal [5-8]. We have employed diffusion coefficients of H for all metals examined here, because no data for T diluted in H are available. The isotope effects would give uncertainty of factor 2 or below, which might not exceed experimental errors. The calculated amounts of T released within t_1=2 x 10^4 s by eq. (6) are given in Fig. 2 (b) to compare with the experimental data in Fig. 2 (a). One can clearly see that in the case of Ni, the experimental data both for the T release rate (see Fig.1 (b)) and the total released amount agreed quite well with the calculations (compare Figs. 2 (a) and (b)), while the other metals did not fit well. This indicates that only for the Ni case the dissolved T was released by normal diffusion process.

According to eq. (5), diffusion coefficients of T in Fe and Mo are so large that most of T dissolved in both metals at 873K must be released out during cooling down to start the T release experiments. This suggests that the released T from both metals were not in solution sites but likely trapped. For Cu, the diffusion coefficient is not so large but the solubility is very small as Fe and Mo so that the observe release would be caused by trapped one as appeared in very slow decay of the T release in Fig. 1 (a).

To confirm the trapping of T in Cu, Fe and Mo, the change of the surface T concentration determined by TIP, *q(t)*, are compared with the T release rate, *J(t)*, in Fig. 5 for Mo. This clearly shows that the decrease (decay) of the surface T can be represented by the first order reaction. And their temperature dependences allow to determine activation energies of rate constants, *k*, of the first order reaction as 64 kJ mol^{-1}, 72 kJ mol^{-1} and 25 kJ mol^{-1} for Cu, Fe and Mo, respectively, given in Fig. 6. Since the first order desorption is just equivalent to detrapping by the first order kinetics, the activation energies are likely to be detrapping energies.

Thus T release into water from the T loaded metals can be described by two processes, diffusional release of dissolved T and detrapping of trapped T by the first order reaction. In Ni, owing to its large T solubility, the T release was dominated by diffusion of dissolved T, while others, detrapping.

Questions are how large the trapped components compared to the dissolved ones and how they were distributed. Since the TIP technique, unfortunately, detects T within the escaping depth of β electron of T, it seems difficult to determine how much was trapped in the bulk. However, as observed in Fig. 1, the T release rates after 1 x 10^4 s were very small, while the surface T still appreciable. This suggests that the trapping is localized near surface otherwise the T release rate should remain high. The

cause of the surface localized trapping in Cu, Fe and Mo is not clear, but is most probably due to surface oxide with -OT bonds. Machining to manufacturing metal sheets, in particular for Fe and Mo, would bring defects in near surface region, which could work as trapping sites. For Ni, its large T solubility must hinder such surface trapping. The trapping in the bulk shall be examined in future work.

5. Conclusions

Metal sheets of Cu and Ni (fcc), and Fe and Mo (bcc) were loaded with T and then immersed into water to observe T release behavior around room temperatures. The amount of T released into water was quantitatively analyzed by the LSC technique and the changes of the T release rate were determined. During the T release process, the T concentration at the metals surface was also measured by the TIP technique and the change of the surface T concentration with time was examined.

The T release from Ni was well interpreted by simple diffusional release of dissoved T, while the other metals show prolonged release which was not caused by the diffusion but detrapping. The TIP measurements clearly show T localized on the metal surfaces, which are separated from the dissolved ones. And the concentration of surface localized T decreased linearly with the T release rate, suggesting detrapping of

the surface localized T, with detrapping energies of 64 kJ mol^{-1} for Cu, 72 kJ mol^{-1} for Fe and 25 kJ mol^{-1} for Mo. The cause of the surface trapping is not clear, but surface oxide with -OT formation and/or defects produced by manufacturing the metal sheets would be the cause. Since the TIP can not detect T in the bulk, it should be clarified whether the trapping sites are distributed into bulk or not.

It should be noted that if apparent diffusion coefficients were determined using an overall T release process, the determined value would be quite different with the relative amount of the dissolved T and the trapped T, which is likely the cause of very wide scattering of diffusion data for Fe near RT and below. At higher temperature, owing to increase of solubility, the diffusion data converge.

Acknowledgement

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Figure captions

Fig. 1 The T release rate into water determined from the LSC technique for (a) Cu, (b) Ni, (c) Fe and (d) Mo. In each figure, closed circle (●), open square (□) and closed triangle (▲) are experimental data obtained at 303 K, 323 K and 353 K, respectively. The solid (——), dotted (- - - -) and dashed (-·-·-) curves are analytical solution of diffusion equation at 303 K, 323 K and 353 K, respectively.

Fig. 2 (a) The integrated amount of T released from Cu, Ni, Fe and Mo into water within 2 x 10^4 s at 303 K, 323 K and 353 K and (b) the calculated amount of T from the analytical solution within 2 x 10^4 s at 303 K, 323 K and 353 K.

Fig. 3 (a) The geometry of the sample exposed to the TIP and (b) TIP results showing T distribution of the surfaces of the Cu, Ni, Fe and Mo samples at 1 h after the H(T) loading.

Fig. 4 The time sequence of the surface T concentration determined by the TIP technique.

Fig. 5 The relationship between the T release rate against the surface T concentration for the Mo sample.

Fig. 6 The temperature dependence of the reaction rate constant for the T desorption from the surface.

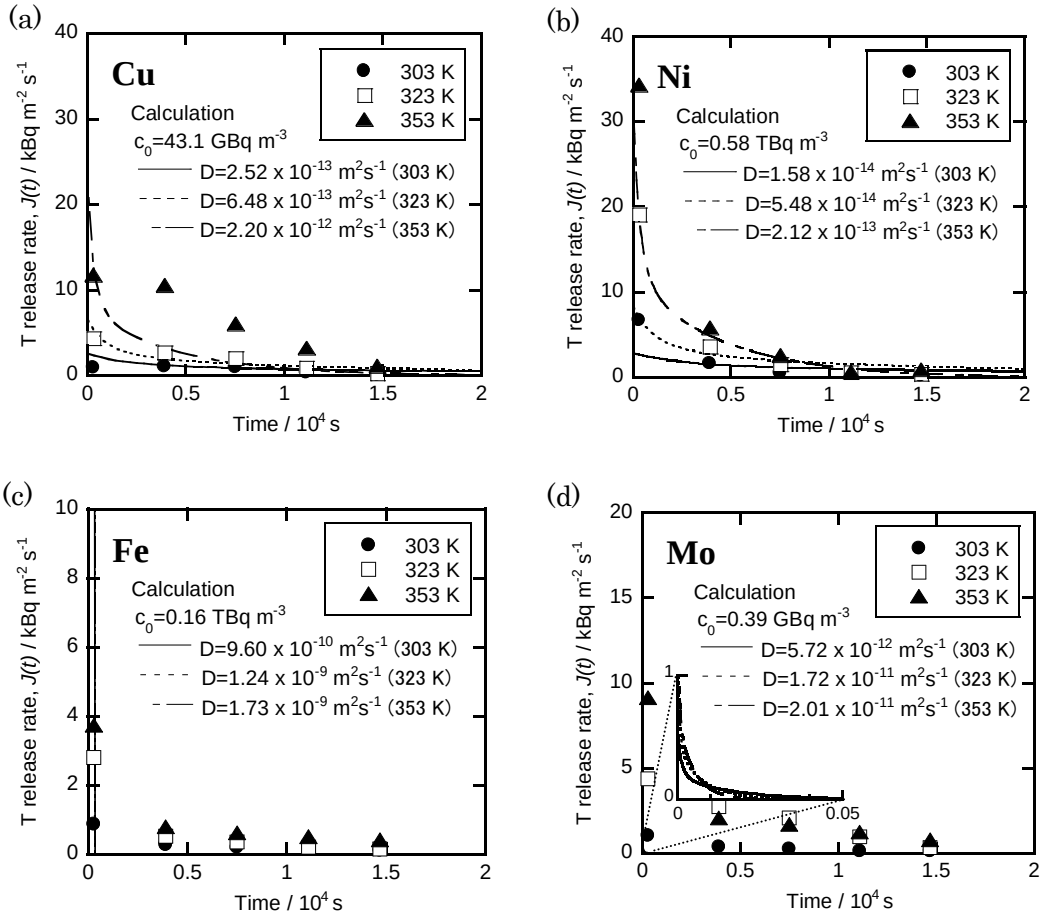

Figure 1

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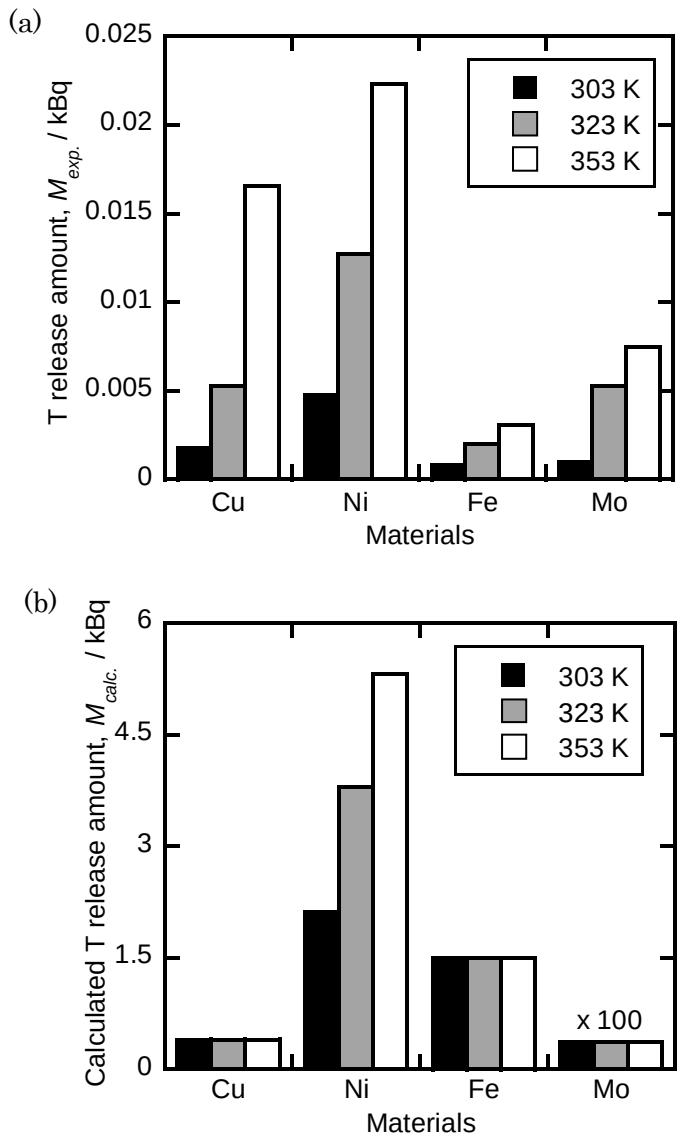

Figure 2

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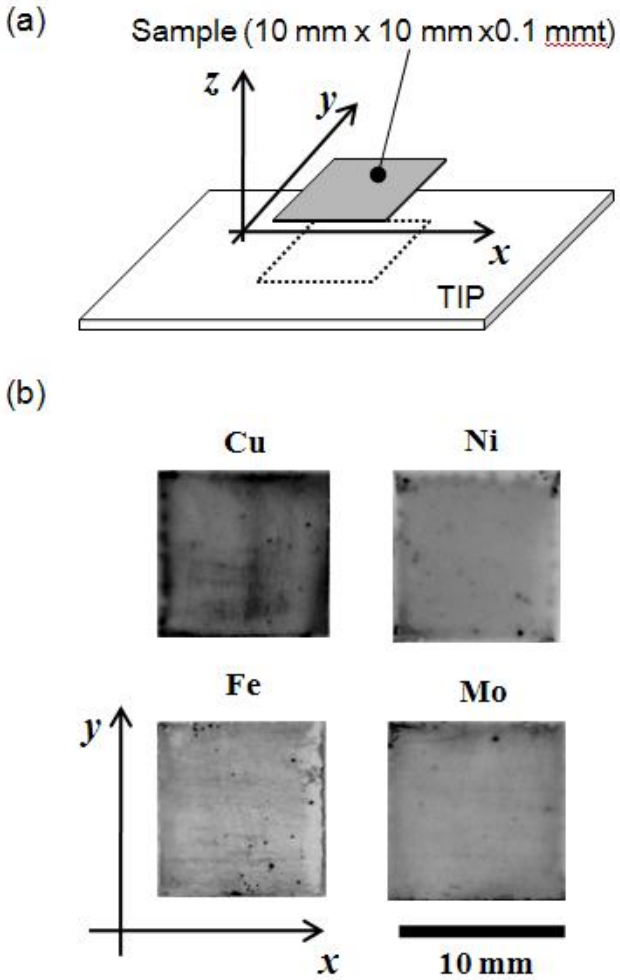

Figure 3

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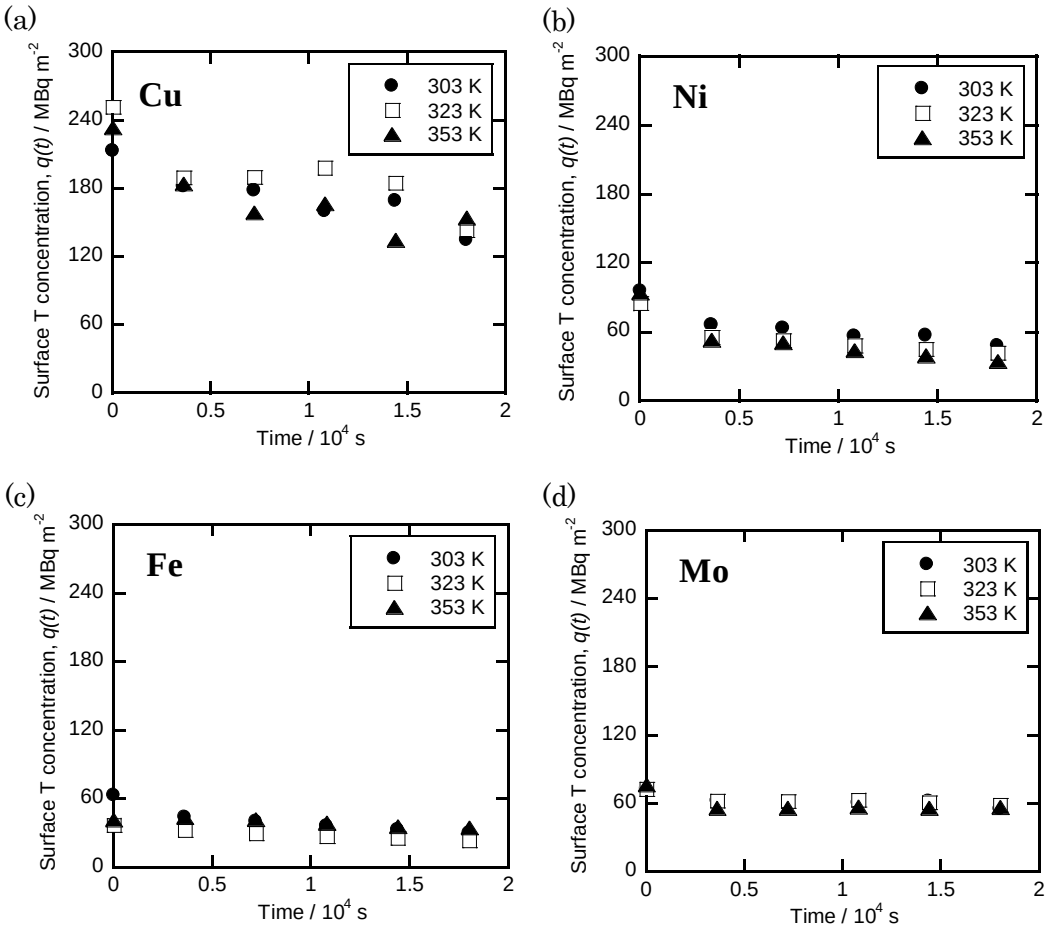

Figure 4

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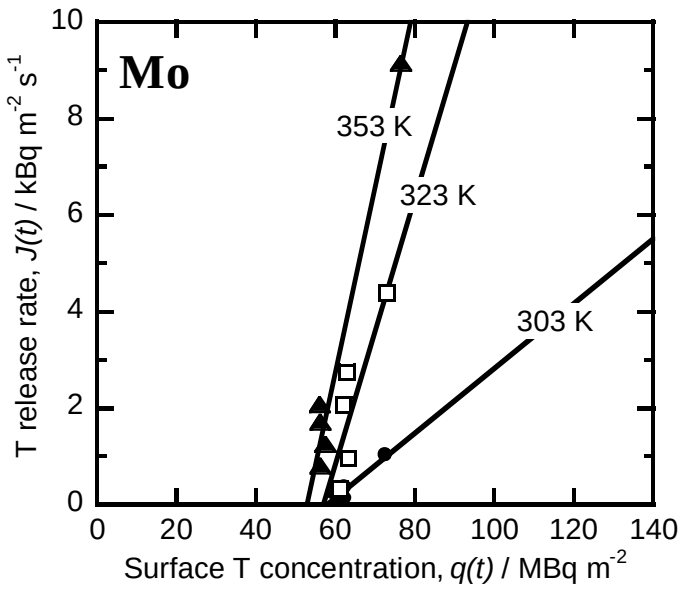

Figure 5

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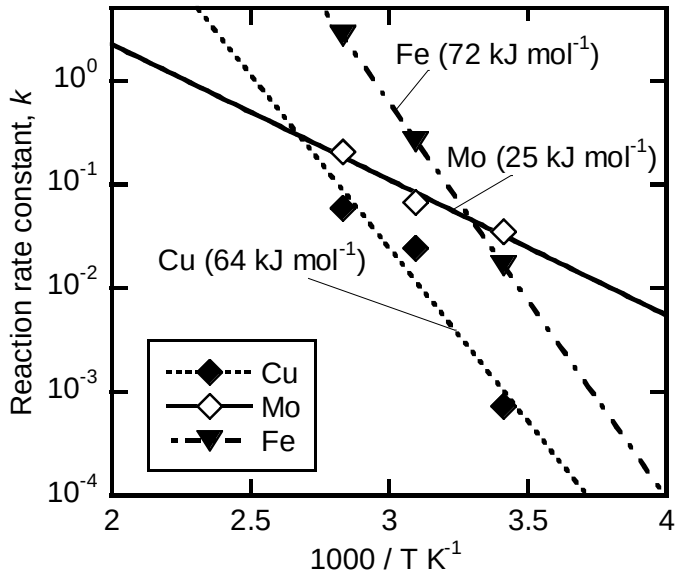

Figure 6

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